



Synthesis of Large-Scale Cadmium Oxide Nanowires from an Aqueous Solution

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Abstract

We report on a simple and template-less technique for growing ultra-long cadmium oxide nanowires on an indium tin oxide (ITO) surface from the aqueous solution. The nanowires, free-standing and with various diameters, are realized on the ITO surface by following a simple hydrothermal reaction of cadmium nitrate and hexamethylenetetramine of a similar molar ratio at 120°C. The nanowires have diameters in the range of 10 to 30 nm and lengths of up to a few tens of micrometers. We identified that the concentration of the solution precursors is crucial to the growth density of the nanowires on the surface but less important to the structural growth (length and geometry) of the nanowires. Such nanowires might possess unique properties that can be used for prospective photonics and optoelectronics materials.

Keywords crystal growth · nanocrystalline materials · microstructure · electronic materials

Introduction

Cadmium oxide (CdO) is a fascinating transition metal oxide material with a wide direct electronic band gap at room temperature, reaching 2.27 eV (contributed by Cd 5s and O 2p transition and indirect electronics band gap of 0.55eV, associated with the Cd 4s and O 2p transition).¹ CdO is the third member in the class of post-transition metal oxides following the series of SnO₂ and In₂O₃ and the second member following the series of ZnO, which exhibits appealing electrical and optical properties.² In the past decade, it has developed into a center of scientific interest owing to its attractive optical properties³ and large optical third-order nonlinearity character,⁴ making it a potential candidate for optoelectronics, solar cells,⁵ gas sensors,⁶ and photocatalysis⁷ applications.

There is a growing interest to explore the fascinating nature of this material, especially related to its low-dimensional (1D or 2D) characteristics. Gulino et al., for instance, investigated the electrical and optical nonlinearity of CdO when prepared in the form of thin films (2D).⁸ They found that they greatly improved the optical nonlinearity properties of CdO when it was prepared as thin films. They attributed such observations to the profound effect of crystal symmetry orientation transformation in CdO, especially from centrosymmetry of the bulk structure to polar symmetry of thin films, which might generate the improvement in their third-order optical nonlinearity. Such results are fascinating and may provide a principal idea to explore the properties of CdO, specifically when their structural growth is constrained into nanowires. There has been an increasing interest in the preparation and analysis of 1D CdO nanostructure.⁹ However, to our best knowledge, to date, few experimental studies reported the growth of CdO nanowires directly on the substrate surface. Since the properties of the material at a reduced-dimension regime greatly depends on their geometrical growth (quantum size effect) and the surrounding medium, an upgraded characteristic and broader application of the CdO nanostructure may be achieved when it is prepared directly on the substrate surface.

In this communication, we present for the first time a simple, seedless, surfactant-less approach to grow CdO nanowires on an indium tin oxide (ITO) surface. By adopting a

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hydrothermal reaction between cadmium nitrate pentahydrate and hexamethylenetetramine at 120°C for several hours, we can grow a large amount of CdO nanowires on the substrate surface. The present approach is extremely simple and rapid to realize large-scale nanowires on the substrate surface. It has been widely reported that the hydrothermal method is versatile for preparing a wide variety of metal-oxide nanostructures that range from ZnO¹⁰ to WO₃¹¹, MnO₂,¹² and ZnS.¹³ The specialty of the present study is that we realized the nanowires on the substrate via effective sequential nucleation and growth on the substrate surface, instead of a seed-assisted growth process as adopted in the recent literature.^{14,15} CdO nanowires should find application in solar cells, optoelectronics and sensing devices.

Experimental

In preparing CdO nanowires, we simply used two chemicals, cadmium nitrate and hexamethylenetetramine. Cadmium nitrate pentahydrate (Cd(NO₃)₂·5H₂O) and hexamethylenetetramine (HMT) were purchased from Aldrich Chemical and used directly without further purification. We prepared an aqueous solution of these chemicals utilizing ultrapure water obtained from Autopure WR600A, Yamato Co., Ltd with resistivity > 18.2 MΩ. In a typical experimental procedure, we prepared a 0.1 M mixed solution of Cd(NO₃)₂ and HMT with a 1:1 molar ratio and then transferred 5 mL of the solution into a clean glass test tube for the growth process.

A piece of ultrasonicated-clean ITO on a glass substrate with dimensions of ca. 1 cm x 1cm was then put into the solution vertically. The reaction was controlled at 120°C for 2 h by transferring the solution into a regular laboratory oven. After the reaction was complete, a white film product on the ITO surface was obtained. We then washed the sample with a copious amount of pure water to remove any residual salt on the surface and dried for 30 min in air at 100°C.

Results and Discussion

We have grown the CdO nanowires on the ITO substrate surface. Field emission scanning electron microscopy (FESEM), JSF 7400F JEOL, Japan, was used to study the structural growth of the nanowires. Figure 1 shows a typical FESEM image of CdO nanowires prepared from the 0.1 M precursor solution that was grown for 2 h. We found that a large number of very long CdO nanowires were successfully realized on the ITO surface (Fig. 1a). The high-magnification image of the CdO nanowires reveals that they possess a variable diameter between 10 and 30 nm and lengths in the range of tens of micrometers (Fig. 1b). It was also observed

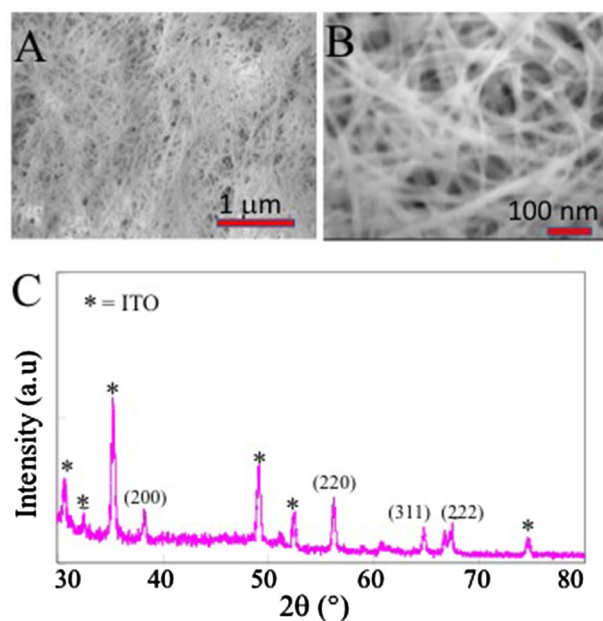


Fig. 1 (a–b) Typical FESEM image of CdO nanowires growth on the ITO surface using precursor concentration of 0.1 M. The ratio between cadmium nitrate and HMT is 1:1. (c) X-ray diffraction spectrum of CdO nanowires.

that the vast majority of the nanowires were free standing without colliding or branching. We performed X-ray diffraction (XRD) experiments on the sample to evaluate their phase crystallinity. The result is shown in Fig. 1c. The diffraction pattern is well matched with the standard diffraction data for CdO (JCPDS File no 05-0640) and we can associate the obtained peaks with (200), (220), (311) and (222) Bragg planes, confirming the sample is a pure phase CdO. Along with the CdO diffraction peaks, the result also indicates the presence of diffraction from the substrate background.

The effect of precursor concentration on the structural growth of CdO nanowires under a constant molar ratio between Cd(NO₃)₂ and HMT was also carried out. We observed that the concentration of the solution precursors seemed to have no significant effect on the structural growth of the CdO nanowires. Instead, the density of the nanowires on the surface decreased with decreasing the concentration of the solution precursor instead (Fig. 2). We also found that the diameter of the nanowires decrease with the decrease of source solution concentration.

While the structural growth is independent of the total precursor concentration under a fixed ratio, it shows a strong dependence on the HMT concentration in the reaction. Under a fixed cadmium nitrate concentration, i.e. 0.1 M, CdO nanostructure growth increases in compactness and dimensions with the increase of HMT concentration (Fig. 3). At a low HMT concentration, for example, 0.02 M, the morphology of the CdO nanostructure was rod-like (Fig. 3a). It

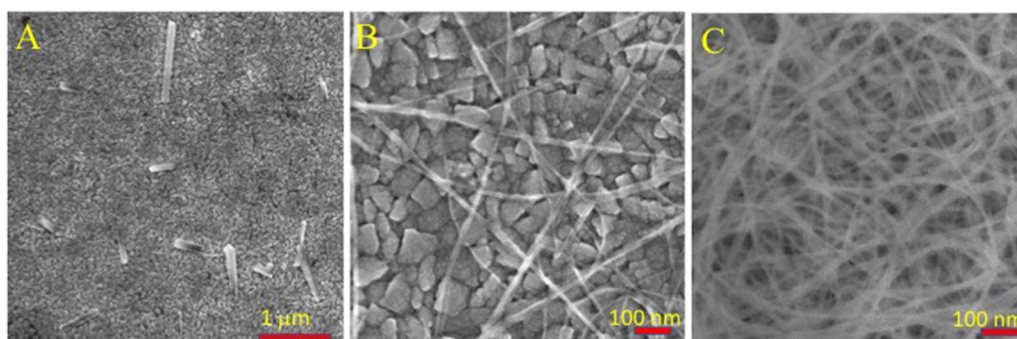


Fig. 2 Typical FESEM image of CdO nanowires grown on the ITO surface prepared using different solution concentrations, namely 0.001 (a), 0.004 (b), and 0.1 M (c). The molar ratio between the reagents in the solution was unchanged. The growth reaction time was 2 h.

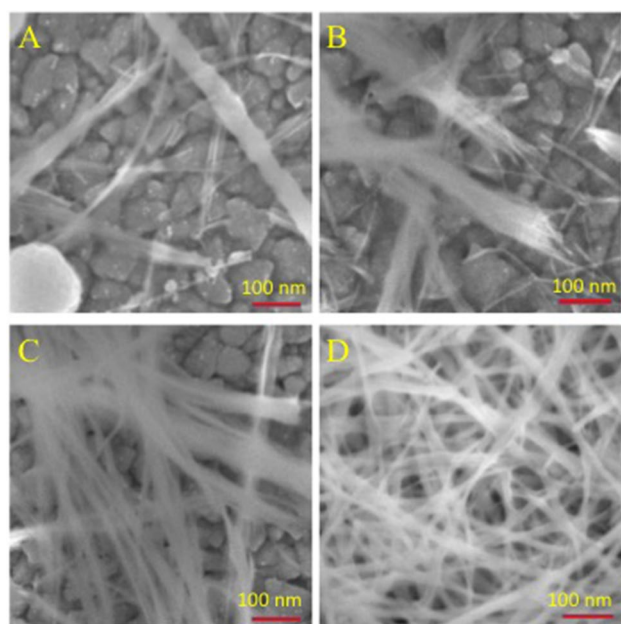


Fig. 3 Structural growth of CdO nanowires under different HMT concentrations. (a) 0.02, (b) 0.05, (c) 0.07 and (d) 0.1 M. Cadmium nitrate was fixed at 0.1 M. The growth reaction was 2 h.

then changed to belt-like and then finally to nanowires with the increase of the HMT concentration (Fig. 3b–d).

We also evaluated the nanostructure byproducts that were grown in the bulk solution to further verify that nanowire formation is merely because of the unique crystal growth process on the substrate surface. The result is shown in Fig. 4. As the figure reveals, the products are irregular-shaped nanostructures. The FESEM analysis results also indicate the formation of large and micro-sized structure in the byproduct that is formed in the bulk solution.

We believe that the mechanism behind the formation of CdO nanowires is the result of a profound effect of HMT in the reaction. Under a high-temperature hydrothermal reaction, the metal cations were reduced from the cadmium salt precursor

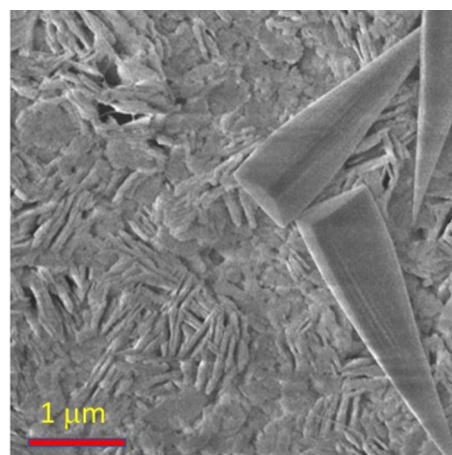


Fig. 4 FESEM image of nanostructures byproduct that are formed in the bulk solution.

and coordinated with oxygen to creating the cadmium oxide. In this process, we predict that the anisotropic growth of CdO system might be because of a stacking effect of the reduced-metal cations toward the principal axis of the CdO crystal, driven by an ample amount of tetradentate amine-metal complex of HMT in the solution. HMT is a cage-like molecule that has a high-symmetry characteristic of cubic space group $I\bar{4}3m$ ¹⁶ with a repeating unit of three atoms fragment of C-NH at the molecular body. Because of the inherent high-affinity nature of the amine group toward metal atoms, it may function as nucleation sites for the reduced-metal systems and directing agent for 1D crystal growth. A similar process has been shown in the synthesis of the 1D system of ZnO¹⁷ and TiO₂¹⁸ systems.

Conclusions

We pointed out that large-scale CdO nanowires of micrometers in length can be easily synthesized by applying a simple hydrothermal reaction of cadmium nitrate and

hexamethylenetetramine of similar molar ratio at a moderately high temperature, 120°C. By varying the concentration of the solution precursors, we can synthesize nanowires with variables lengths and diameters. The nanowire is potential material for application in nonlinear optics, optoelectronics and computing devices and is a prospective nano-template for growing other low-dimensional materials systems.

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Conflict of interest The authors declare that they have no conflict of interest in this work.

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